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(19) (CA) **CANADIAN PATENT** (12)

(54) Process for the Production of Titanium Dioxide

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A process for the production of titanium dioxide

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10 The present invention relates to a process for the  
production of titanium dioxide by discontinuous digestion  
of titanium slag with sulphuric acid, production of a  
titanyl sulphate solution suitable for hydrolysis from the  
solid digestion cake obtained during digestion, hydrolysis  
15 of the titanyl sulphate, separation and calcination of the  
titanium-containing hydrolyzate, evaporation of the waste  
acid separated from the hydrolyzate and re-use of the  
sulphuric acid separated from the evaporated waste acid  
in the digestion of titanium slag.

20 The requirement for recycling of sulphuric acid from  
the  $TiO_2$  production process by the sulphate process is  
having to be met more and more. In addition to the  
expected economic disadvantages in comparison with dumping  
of waste acid in the ocean, the process often encounters  
technical problems.

25 A process for working up waste acids is known from  
DE-A 3 327 769 and is adopted on an industrial scale. De-  
pending on the local condition, however, problems can  
arise here if the waste acid is to be almost completely  
recycled.

30 According to the working up process currently  
adopted, the waste acid is concentrated, preferably by  
multi-stage vacuum evaporation, until a 60 to 70%  
sulphuric acid with a low content of dissolved metal  
sulphates can be separated by filtration from crystal-  
lized metal sulphates.

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5 Weinheim 1979). However, this stage of the process is extremely expensive with respect both to the investment costs and to the energy and maintenance costs.

It is accordingly the object of the present invention to propose a method which overcomes the above-mentioned disadvantages of the prior art in an economical manner.

10 This object can surprisingly be achieved by the following combination of measures:

- evaporation of the 60 to 75% sulphuric acid separated from the metal sulphates and containing dissolved metal sulphates under vacuum in horizontal or circulation evaporators at from 120 to 190°C to 76 to 87%  $H_2SO_4$  (based on salt-free sulphuric acid),
- 15 mixing of the ground titanium slag with 95 to 98% sulphuric acid at from 30 to 80°C and addition of the recycled acid at a temperature of from 80 to 190°C, 20 preferably from 100 to 160°C.

The present invention accordingly relates to a process for the production of titanium dioxide by discontinuous digestion of titanium slag with sulphuric acid, 25 production of a titanyl sulphate solution suitable for hydrolysis from the solid digestion cake obtained during digestion, hydrolysis of the titanyl sulphate, separation and calcination of the titanium-containing hydrolyzate, evaporation of the waste acid separated from the hydro- 30 lyzate and re-use of the sulphuric acid separated from the evaporated waste acid in titanium slag digestion, a 60 to 75% pre-concentrated sulphuric acid being separated from the solid metal sulphates and hydrogen sulphates after

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5 In a particularly desirable embodiment of the process according to the invention, the concentration of the sulphuric acid is advantageously between 87 and 91%, preferably 88 and 90%  $H_2SO_4$  (calculated as solids-free and salt-free acid) at the start of the digestion reaction and  
10 from 35 to 70% of the required sulphuric acid is recovered as recycled acid from the process.

The necessary temperatures of the fresh acid and the recycled acid can be lowered according to the invention by grinding the titanium slag more finely.

15 The production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is preferably carried out by evaporation at from 120 to 190°C and from 40 to 150 mbar.

Horizontal evaporators with tantalum heat exchangers or circulation evaporators are particularly suitable for  
20 these evaporation processes not only for reasons of energy consumption.

Valuation of the process according to the invention has to consider the fact that secondary energy can be used  
25 instead of primary energy for producing the recycled acid and that the investment and maintenance costs are substantially lower compared with the prior art.

The drawing serves to illustrate the process according to the invention.

30 The fresh acid (1) required for the digestion of raw material is mixed in the digestion reactor (3) or in a preceding mixer with the ground titanium slag (2) (optionally with addition of ground ilmenite). The fresh acid should have a temperature of from 30 to 80°C,  
35 preferably from 50 to 80°C. The necessary quantity of

5 The metal sulphates are partly in the form of  
hydrogen sulphates and contain 60 to 75% sulphuric acid  
as moisture. It is therefore advantageous to decompose  
this "filter salt" thermally with formation of  $\text{SO}_2$  and to  
10 produce therefrom the 95 to 98% sulphuric acid required  
as fresh acid. However, reaction with Ca compounds (DE-A  
3 327 770) or a different harmless elimination process is  
also possible.

Sulphuric acid losses occur mainly through the filter  
salt, but also through the moisture of the solid residues  
15 resulting from raw material digestion, the sulphuric acid  
bound in the  $\text{TiO}(\text{OH})_2$  and the unavoidable waste water. As  
pre-concentrated acid, therefore, only about 40 to 60% of  
the sulphuric acid used during digestion can be recovered.  
With 60 to 75%  $\text{H}_2\text{SO}_4$ , however, the concentration of this  
20 acid is too low to allow autothermal slag digestion in  
mixture with the necessary amount of from 95 to 98% fresh  
acid.

The pre-concentrated acid (15) which still contains  
about 3 to 6% by weight of dissolved metal sulphates  
therefore must be evaporated in an evaporation II (16) to  
25 76 to 87%  $\text{H}_2\text{SO}_4$  (as salt-free acid), before it can be  
recycled (17) for the digestion of the raw material. The  
evaporation II (16) is carried out according to the inven-  
tion by vacuum evaporation at 120 to 190°C. Circulation  
evaporators or horizontal evaporators with tantalum heat  
30 exchangers can be used as evaporator systems. Horizontal  
evaporators are preferred owing to the particularly high  
specific evaporation capacity (with respect to the  
tantalum heat exchanger surface). Preheating of the pre-

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Example 1 (Comparison Example)

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17.5 t of ground titanium slag were mixed with 18 t of metal sulphate-containing recycled acid and with 13.6 t of fresh 96% sulphuric acid (20°C). The digestion reaction was initiated by addition of 1.4 t of water and introduction of 0.6 t of steam. The maximum reaction temperature of 203°C was attained after 10 minutes. After initiation of the reaction, air was blown through the mixture (for 30 minutes at 350 m<sup>3</sup><sub>n</sub>/h, then for 7 hours at 20 m<sup>3</sup><sub>n</sub>/h). After a maturing time of 7 hours, the digestion cake had a temperature of 169°C. The TiO<sub>2</sub> yield was 95.3%.

The digestion cake was dissolved with a proportion of the sulphuric acid-containing waste water from the hydrolyzate filtration (5.4% by weight H<sub>2</sub>SO<sub>4</sub>). After working up the titanyl sulphate solution, the mixture was hydrolysed using a further proportion of the sulphuric acid-containing waste water as diluent water.

85 t of waste acid containing 23.2% H<sub>2</sub>SO<sub>4</sub> and 29.8% SO<sub>4</sub><sup>2-</sup> (total) were separated from the hydrolyzate filtration process. The waste acid was evaporated in a 2-stage vacuum evaporator until the sulphuric acid (calculated as salt-free acid) had a concentration of 66% H<sub>2</sub>SO<sub>4</sub>. 31 t of 5 bar steam were used up for evaporating 47.5 t of H<sub>2</sub>O.

11.3 t of sulphuric acid-containing filter cake were separated from the metal sulphate-sulphuric acid suspension after cooling to 55°C. The pre-concentrated acid (25.7 t) contained 62.8% of H<sub>2</sub>SO<sub>4</sub>, 32.4% of H<sub>2</sub>O and 4.8% of dissolved metal sulphates.

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5 being 160°C. The steam consumption for producing 20.0 t  
of recycled acid was 10 t of 15 bar steam. The 1.3 bar  
steam for preheating the pre-concentrated sulphuric acid  
was produced by depressurising the 15 bar steam conden-  
sate. In view of the re-use of the 120°C hot steam  
10 condensate for steam production, the energy consumption  
for producing the recycled acid from pre-concentrated acid  
was 22,700 kJ. 0.6 t of 5 bar steam were also saved when  
initiating the digestion reaction. An advantage of 33% of  
the energy requirement was therefore achieved in compari-  
son with the prior art.

### 15 Example 3

17.5 t of ground titanium slag were mixed with 13.6 t  
of fresh 96% sulphuric acid (75°C). The digestion reaction  
was initiated by addition of 20.76 t of recycled acid  
20 (77.65% of  $\text{H}_2\text{SO}_4$ , 16.57% of  $\text{H}_2\text{O}$ , 5.78% of  $\text{MeSO}_4$ , corre-  
sponding to 82.4% of  $\text{H}_2\text{SO}_4$  in the salt-free acid) having  
a temperature of 140°C. Air ( $350 \text{ m}^3_{\text{n}}/\text{h}$ ) was blown through  
the reaction composition until the maximum temperature of  
192°C was attained after 14 minutes. 5 bar steam (180°C,  
25 0.3 t/h for 20 minutes and 20 kg/h for a further 7 hours)  
was then blown through the reaction composition. After  
stopping the steam, the temperature of the digestion cake  
was 172°C and the  $\text{TiO}_2$  yield was 95.2%.

The remainder of the process was carried out as in  
30 Example 1. Evaporation II during which 25.7 t of pre-  
concentrated acid were evaporated to 20.76 t of recycled  
acid was carried out at 60 mbar in the same horizontal  
evaporator as in Example 2. The pre-concentrated acid

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Table 1

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Exp. Fineness of grinding		T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>	t
No.	% by weight <40 μm	[°C]	[°C]	[°C]	[°C]	[min]
10	1	81	50	110	76	-
	2	81	50	140	91	106
	3	81	70	140	101	154
	4	81	80	140	109	193
	5	81	70	160	117	192
15	6	100	50	120	86	168
	7	100	50	140	95	185

20 The experimental results show that the temperature of the recycled acid can be lower if the titanium slag is ground more finely (Experiment 7) than with a coarser grinding (Experiment 2) achieving approximately the same reaction rate. Also the temperature of the 96% fresh acid can obviously be lowered instead of the temperature of the recycled acid.

25 The slower rise in the temperature of the laboratory digestions in comparison with the rise in temperature on an industrial scale is due to the relatively high thermal losses.

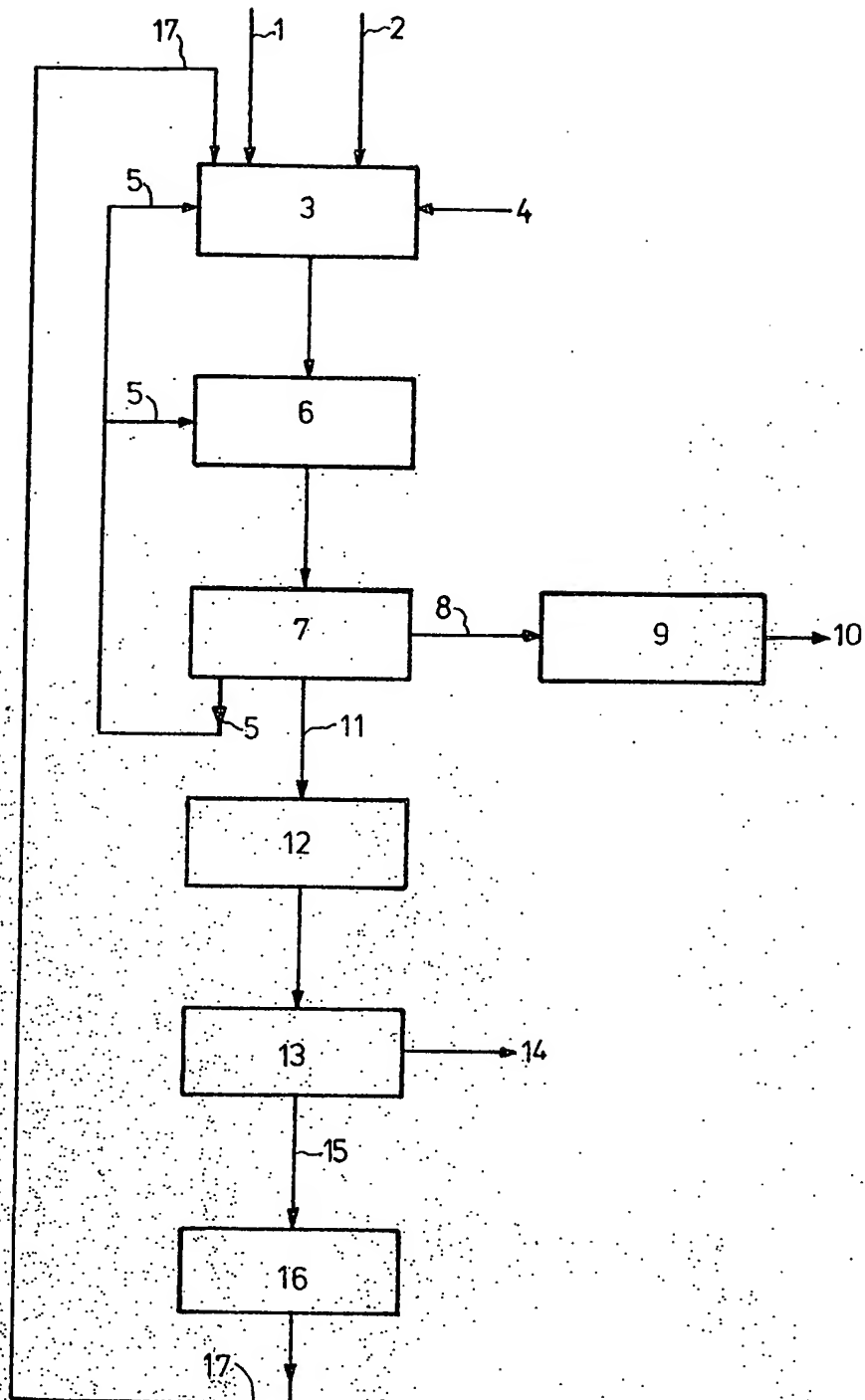
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5. A process according to claim 1, 2 or 3, wherein the digestion reaction is initiated by addition of hot 76-to 87%-sulphuric acid ("recycled acid") at from 100 to 160°C.
6. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 87 and 91%,  $H_2SO_4$  (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
7. A process according to claim 1, 2 or 3, wherein the concentration of the sulphuric acid is between 88 and 90%  $H_2SO_4$  (calculated as solids-free and salt-free acid) at the beginning of the digestion reaction and from 35 to 70% of the sulphuric acid required is recovered from the process as recycled acid.
8. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar.
9. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric acid is effected by evaporation at from 120 to 190°C and from 40 to 150 mbar and a horizontal evaporator with a tantalum heat exchanger is used as evaporator.
10. A process according to claim 1, 2 or 3, wherein the production of the 76 to 87% acid from 60 to 75% pre-concentrated sulphuric



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